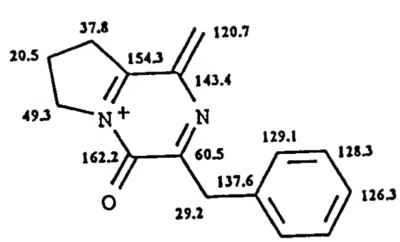
^{13}C NMR data



^{1}H NMR data

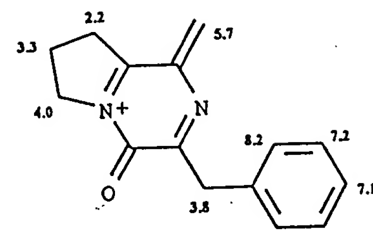


Figure 1: Structural formula of the product of the intramolecular cyclisation of H-Phe-Pro-pyridinium methyl ketone. The characteristic chemical displacements (in ppm) determined by means of ^{13}C NMR and ^{1}H NMR are assigned to the corresponding atoms.

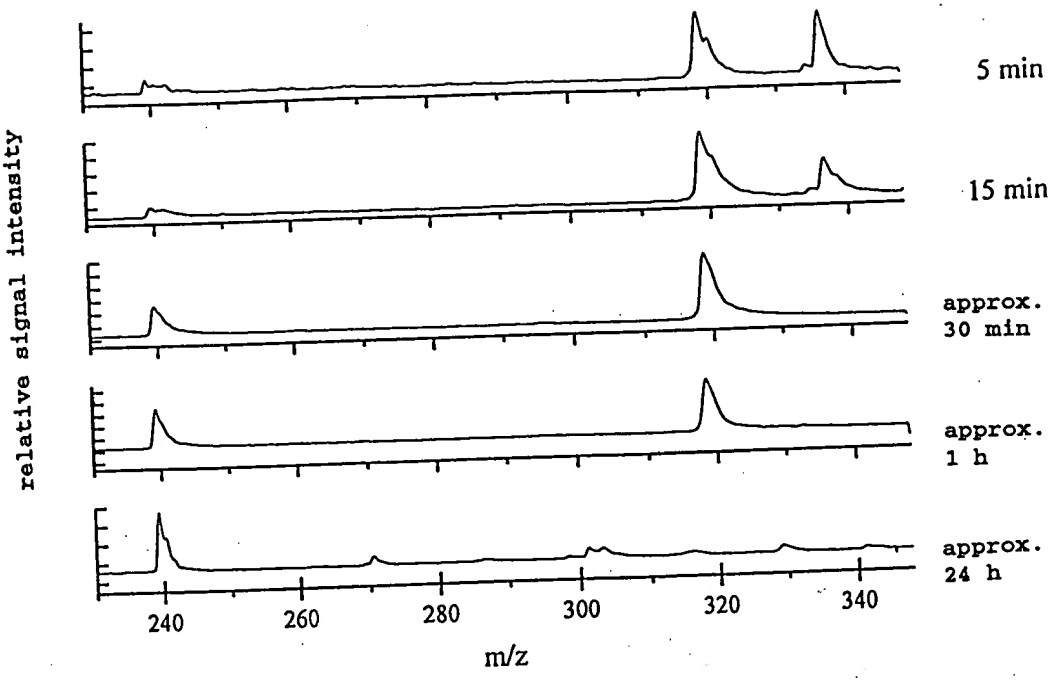


Figure 2: MALDI-TOF mass spectra of the cyclisation of H-Phe-Pro-pyridinium methyl ketone in an aqueous buffer solution pH = 7.6, recorded according to the incubation period.

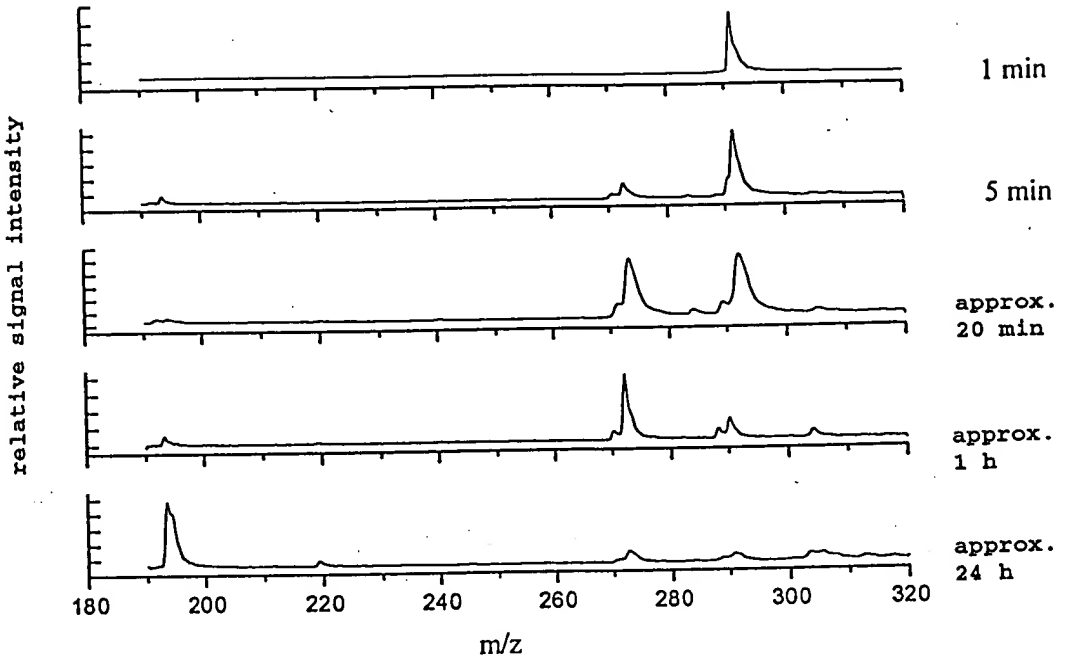


Figure 3: MALDI-TOF mass spectra of the cyclisation of H-Val-Pro-pyridinium methyl ketone in an aqueous buffer solution pH = 7.6, recorded according to the incubation period.

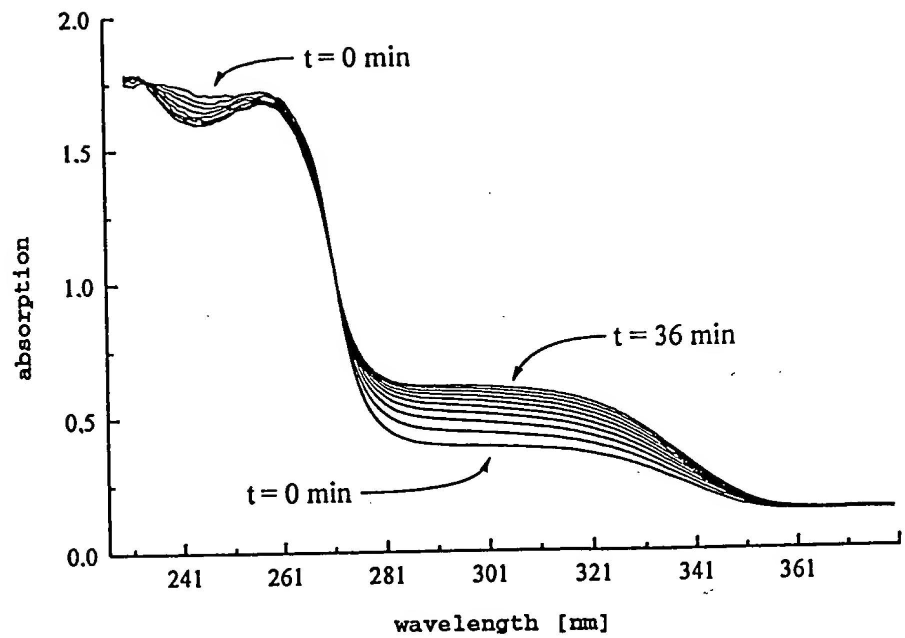


Figure 4: UV spectra of an aqueous solution of H-Phe-Pro-pyridinium methyl ketone incubated in 0.1M HEPES buffer, pH = 7.6, at 30°C. The cyclisation reaction was monitored over a period of 40 minutes.

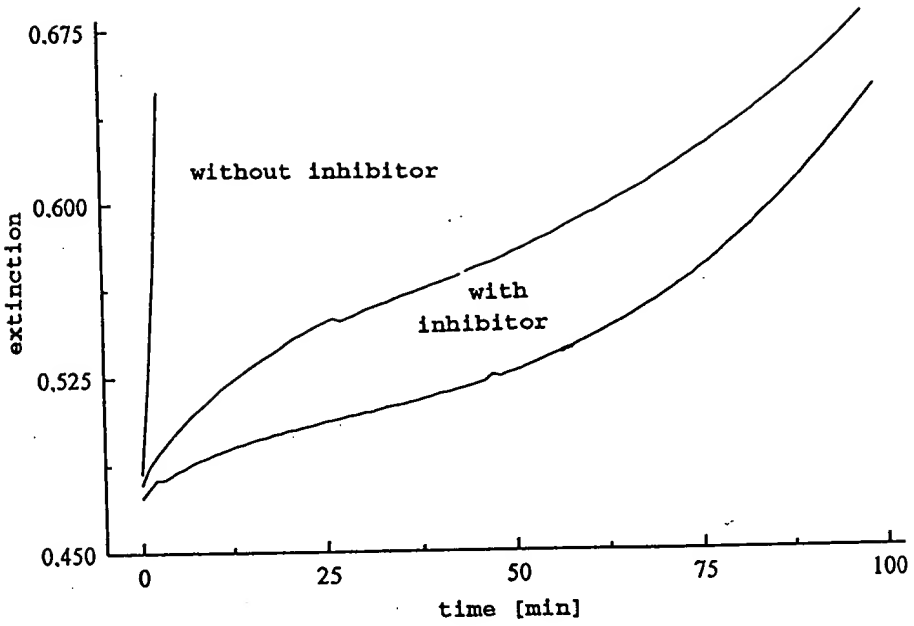


Figure 5: Progress curves of the DP IV-catalysed hydrolysis of the substrate H-Gly-Pro-*p*NA in the presence of 2.8×10^{-3}M H-Val-Pro-pyridinium methyl ketone, 0.06 µg/ml of DP IV, 4×10^{-4}M H-Gly-Pro-*p*NA in the batch, 0.1M HEPES buffer, pH = 7.6, 30°C.

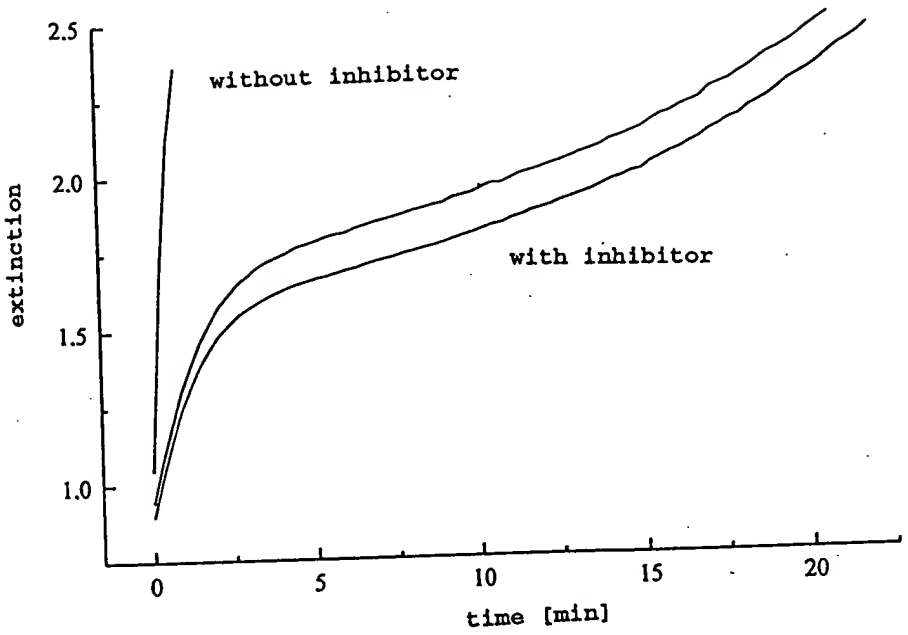


Figure 6: Progress curves of the DP IV-catalysed hydrolysis of H-Gly-Pro-*p*NA in the presence of 2.1×10^{-4}M H-Phe-Pro-pyridinium methyl ketone, 0.06 µg/ml of DP IV, 1.0×10^{-3} mol/litre of H-Gly-Pro-*p*NA in the batch, 0.1M HEPES buffer, pH = 7.6, 30°C.

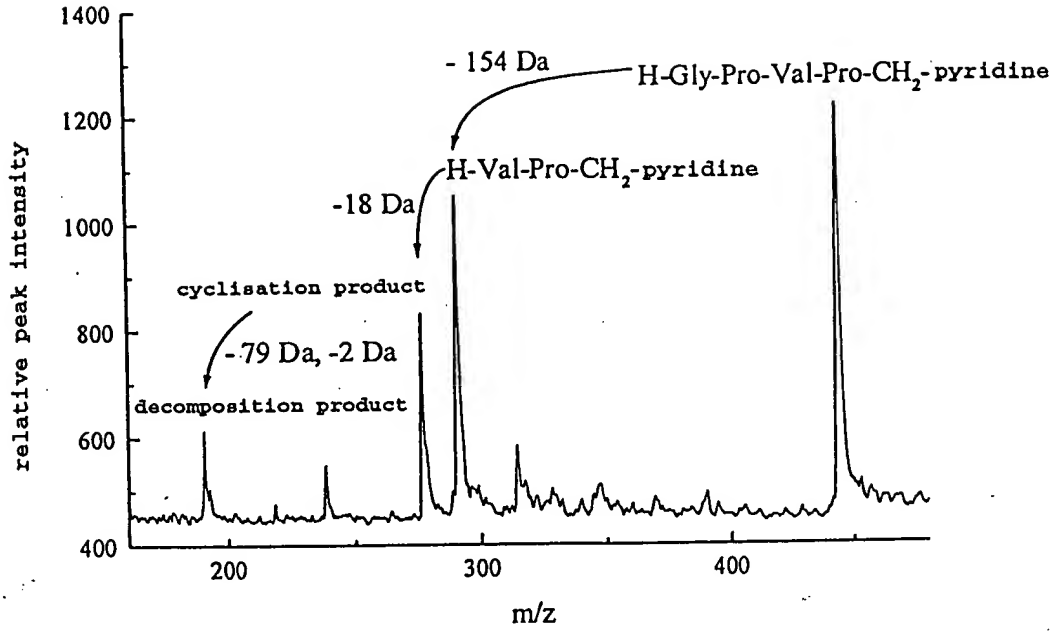


Figure 7: MALDI-TOF mass spectrum of the incubation batch of the DP IV-catalysed hydrolysis of H-Gly-Pro-*p*NA in the presence of 2.6×10^{-5} mol/litre of H-Gly-Pro-Val-Pro-pyridinium methyl ketone, 0.06 µg/ml of DP IV, 2.0×10^{-4} mol/litre of H-Gly-Pro-*p*NA, 0.1M HEPES buffer, pH = 7.6, 30°C. Recorded after an incubation period of 60 minutes.

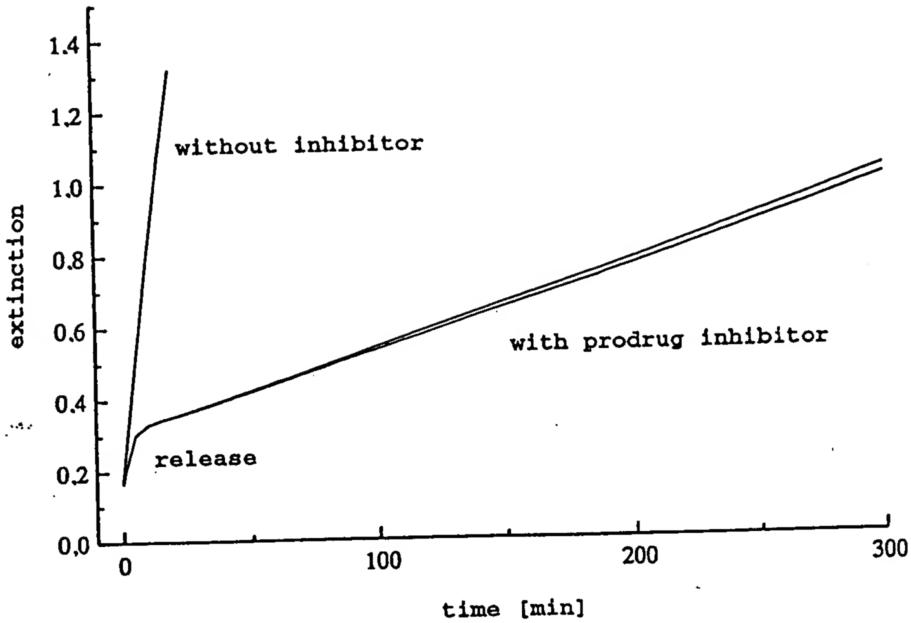


Figure 8: Progress curves of the DP IV-catalysed hydrolysis of H-Gly-Pro-*p*NA in the presence of 2.6×10^{-5} mol/litre of H-Gly-Pro-Val-Pro-pyridinium methyl ketone, 0.06 µg/ml of DP IV, 2.0×10^{-4} mol/litre of H-Gly-Pro-*p*NA in the batch, 0.1M HEPES buffer, pH = 7.6, 30°C.